NSC-261

Photochemical Equilibrium Studies of Carbon Dioxide and Their Significance for the Venus Atmosphere[1]

Robert R. Reeves, Jr., Paul Harteck, Barbara A. Thompson, and Roger W. Waldron

Department of Chemistry

Rensselaer Polytechnic Institute

Troy, New York

---

(1) Presented in part at the 150th A.C.S. National Meeting, Atlantic City, N.J., September 1965

Abstract

The photolysis of carbon dioxide has been studied using the 1633 A persistent line of bromine. Dissociation into carbon monoxide and oxygen accompained by formation of ozone was readily observed. The O_3/O_2 ratio was comparable to that obtained on irradiation of oxygen alone. The addition of traces of moisture to the system resulted in a recombination back to CO_2. With moisture content of about one part in a thousand the recombination to CO_2 was virtually complete. This was true with either excess CO or excess O_2. The system was studied at various temperatures from 25° C to -72° C beginning with pure CO_2 or with mixtures of CO and O_2. The mechanism for recombination in the presence of traces of H_2O may involve reactions such as:

$$CO + OH \rightarrow CO_2 + H$$

$$CO + HO_2 \rightarrow CO_2 + OH$$

The addition of small amounts of H_2 also inhibits the dissociation of CO_2, tending to confirm the proposed mechanism. These results may

contribute substantially to an understanding of the chemistry of the Venus atmosphere.

Introduction

The photochemistry of carbon dioxide has been studied for many years and has become of special interest more recently in connection with the chemistry of the Venus atmosphere. Groth[2] in 1937 and others

(2) Groth, W., Z. phys. Chem. B37, 307 (1937)

in recent years[3,4,5,] have carried out investigations using the 1470 A

(3) Jucker, H. and Rideal, E.K., J. Chem. Soc. 1957, 1058.
(4) Mahan, B.H., J. Chem. Phys. 33, 959 (1960)
(5) Warneck, P., Disc. Faraday Soc. 37, 57 (1964)

line of xenon. Warneck[5] has also utilized the 1236 A line of krypton and a hydrogen lamp emitting in the 1600 A region. Some questions still exist, however, as to the exact nature of the processes occurring in the photolysis. In particular, some workers have reported finding smaller amounts of oxygen produced than expected. The bromine lamp, recently developed in this laboratory[6], provides a high output intensity at

(6) Thompson, B.A., Reeves, R. R., Jr. and Harteck, P., J. Phys. Chem. 69, 3964 (1965)

1633 A and thus can be used for photochemical equilibrium studies. Since none of the previous studies of carbon dioxide was carried to photochemical equilibrium, it seemed appropriate to investigate this

system with the bromine lamp. This paper describes some results of this investigation.

Experimental

The bromine lamp has been described in detail elsewhere[6]. Features of interest for the present study include the outer cooling jacket which permits irradiation at any desired temperature, the insulating vacuum jacket between the irradiation chamber and the discharge tube, and a provision for withdrawal for analysis of small samples of the gas being irradiated at any time.

The gases used were obtained from Matheson Co. and were purified before use. CO_2 (Coleman Grade) was purified by pumping away air at liquid nitrogen temperature, then separating from any water vapor by distillation at dry ice temperature. CO always contained trace amounts of iron carbonyl which could have interfered with the equilibrium observation. This impurity was therefore removed by bubbling the gas through sodium hydroxide solution and the CO was then dried by passing through liquid oxygen traps. Oxygen, argon, and hydrogen were dried by passing through liquid oxygen traps and used without further purification. Saml amounts of water were introduced when desired by using argon or oxygen directly from the cylinder, eliminating the liquid oxygen traps.

Irradiations were carried out on pure CO_2; mixtures of CO_2 and argon; mixtures of CO, O_2 and argon; and on mixtures of CO_2, H_2, and argon. Argon served as a mass spectrometer reference and, in the case of the CO-O_2 mixtures, to lower the explosion limits. Most irradiations were performed at room temperature, but experiments were also

made at -31°C and -72°C. Gas samples were analyzed using a Consolidated Electrodynamics Corp. 21-130 mass spectrometer.

Where desirable, ozone was measured by bubbling the irradiated gas through potassium iodide solution and titrating the liberated iodine with standard sodium thiosulfate.

Results

Irradiation of CO_2

When pure CO_2 was irradiated, dissociation occurred resulting in the formation of CO and O_2. O_3 was also present and the O_3/O_2 ratio was comparable to that obtained with pure O_2.[6] The ratio of CO to O_2 was measured mass spectrometrically and, including the oxygen from the O_3, was found to be 2:1 in contrast to the results of some other workers[5] who have reported finding less than the stoichiometric amount of oxygen.

In all cases (about 20 experiments) the dissociation proceeded initially at a rate consistent with a quantum yield of one for CO_2 decomposition as determined by comparing the rate with the rate of ozone formation in a flowing system of pure O_2[6]. This initial rate was maintained until a few percent of the CO_2 had been decomposed. Back reactions then began to compete and a steady-state equilibrium was approached. A typical curve of CO/CO_2 ratio as a function of irradiation time is shown in Figure 1. This curve shows a CO/CO_2 ratio at equilibrium of about 0.13. However, although the initial rate of decomposition was always the same, the position of the equilibrium seemed to be rather erratic, ranging from a CO/CO_2 ratio of about 0.1

to about 0.35 (O_2/CO_2 ~ 0.05 - 0.18). The value of 0.35 for CO/CO_2 was the maximum obtained in these experiments.

Irradiation of $CO-O_2$ Mixtures

In an effort to understand the variable equilibrium decomposition observed with pure CO_2, it was decided to approach the equilibrium from the opposite direction, i.e., beginning with mixtures of CO and O_2. All these experiments were done with a CO pressure of less than 150 mm. The initial O_2 pressure was varied from 50 to 100 mm and argon was added to bring the total pressure into the 650 mm region. In all cases it was found that reaction to form CO_2 proceeded to completion. With excess CO, all the O_2 was consumed ($O_2/CO_2 < 0.005$) and with excess O_2, all the CO was consumed ($CO/CO_2 \lesssim 0.01$). A close examination of the mass spectra revealed the presence of small amounts of water vapor (~0.1%).

When the reaction gases were dried as carefully as possible (~0.01% H_2O) the equilibrium was shifted slightly in the direction of increased decomposition (O_2/CO_2 ~ 0.03) and thus it was concluded that the reaction to form CO_2 was being catalyzed due to the presence of water. The fact that no higher degree of dissociation was obtained starting with $CO-O_2$ mixtures was probably due to the presence of minor traces of hydrogen-containing impurities in the CO.

Irradiation of CO_2 with H_2 Added

To gain further insight into the nature of the recombination reactions, irradiations were carried out on pure CO_2 to which traces

of hydrogen were added. This would react with the O-atoms formed by CO_2 dissociation to produce OH radicals and H-atoms. If these are really catalyzing the recombination to CO_2 then the addition of small amounts of H_2 should cause a radical shift in the equilibrium.

It was found that with as little as 0.1% H_2 present, the dissociation of CO_2 was completely inhibited ($O_2/CO_2 < 0.005$). With 0.01% H_2, dissociation occurred to a very small extent ($O_2/CO_2 \sim 0.02$). Thus the assumption of catalysis by water or its decomposition products seems correct. It should be noted that most of the added hydrogen remained in the form of H_2, as could be observed mass spectrometrically, and only a small fraction was converted to H_2O during the time of irradition.

Discussion

Steady-state equilibrium

When CO_2 is irradiated with ultraviolet light, the following reactions occur and play a major role in defining the position of equilibrium:

$$CO_2 + h\nu \rightarrow CO + O \qquad (1)$$

$$CO + O \xrightarrow{k_2} CO_2 + h\nu \qquad (2)$$

$$O + O_2 + M \xrightarrow{k_3} O_3 + M \qquad (3)$$

$$O + O_3 \xrightarrow{k_4} O_2 + O_2 \qquad (4)$$

$$O_2 + h\nu \rightarrow O + O \qquad (5)$$

$$O_3 + h\nu \rightarrow O_2 + O \qquad (6)$$

An expression for the expected equilibrium ratio of CO to CO_2 can be derived from a steady-state treatment of these reactions. By setting

up steady-state equations for CO_2, O-atoms, and O_3, and combining the three equations, the following two relationships between CO, CO_2, O_2, and O_3 may be obtained:

$$\frac{(O_3)}{(O_2)} = \frac{\alpha_2 k_2 (CO)}{\alpha_2 k_4 (CO_2)} \qquad (I)$$

$$\frac{(CO)}{(CO_2)} = \frac{k_3(M) - k_4(O_3/O_2)}{\frac{\alpha_1 k_2}{\alpha_3}(O_3/O_2)} \qquad (II)$$

where α_1, α_2, and α_3 are the absorption coefficients of O_3, O_2, and CO_2 for the incident radiation. By substitution of (I) into (II), and application of the quadratic formula, the CO/CO_2 ratio is found to be:

$$\frac{(CO)}{(CO_2)} = \frac{-1 + \sqrt{1 + 4\frac{\alpha_1 k_3(M)}{\alpha_2 k_4}}}{\frac{2\alpha_1 k_2}{\alpha_3 k_4}} \qquad (III)$$

By substitution of (III) into (I), the O_3/O_2 ratio is:

$$\frac{(O_3)}{(O_2)} = \frac{-1 + \sqrt{1 + 4\frac{\alpha_1 k_3(M)}{\alpha_2 k_4}}}{2\alpha_1/\alpha_2} \qquad (IV)$$

Equation (IV) is identical with that calculated for the O_3/O_2 ratio in a pure O_2-O_3 system by a similar steady-state treatment[7], showing

---

(7) Harteck, P., Reeves, R.R., Jr., and Thompson, B.A., To be published.

---

that in a CO_2 system at photochemical equilibrium the O_3/O_2 ratio is

independent of the CO_2 and CO.

The reported values of 20, 75, and 2.5 for α_1, α_2, and α_3 at 1633 A[8] were substituted into Equation (III) together with the

(8) Watanabe, K., Zelikoff, M., and Inn, E.C.Y., " Absorption Coefficients of Several Atmospheric Gases", AFCRC Technical Report No. 53-23 (1953).

following values for k_2, k_3, and k_4. At 300°K the respective values were 10^{-18} cc/particle-sec, 10^{-14} cc/particle-sec, and 3×10^{-34} $cc^2/part^2$-sec and at 200°K the values were 10^{-18}, 10^{-14}, and 5×10^{-34}. The value of k_2 is that reported by Mahan and Solo[9] and the same value was used

(9) Mahan, B. H. and Solo, R. B., J. Chem. Phys. 37, 2669 (1962).

at both temperatures because recent work in this laboratory has shown that the heat of activation is very low[10]. Exact values for the rate

(10) Harteck, P., Reeves, R.R., Jr., and Bergendahl, A.S., To be published.

coefficients of Reactions (3) and (4) are not generally agreed upon at present[11]. The above values were selected in the light of the data

(11) For discussion see Kaufman, F. and Kelso, J.R., Disc. Faraday Soc. 37, 26 (1964) and Mathias, A. and Schiff, H.I., Ibid. 37, 38 (1964).

available. In any case the conclusions drawn would not be substantially affected by small changes in the value of k_2, k_3 and k_4. A pressure of

100 mm was assumed for the calculations.

Substitution of these values into Equation (III) gives an equilibrium CO/CO_2 ratio of 52 at 200°K and 28 at 300°K. Thus, under the experimental conditions used for this work the CO_2 should have been over 90% dissociated at equilibrium. Instead, as noted above, the maximum dissociation found was about 25% with evidence that recombination to CO_2 was being catalyzed by water or its decomposition products. It is clear from these results that for equilibrium studies the requirements for purity of systems are even more stringent than had been thought.

Recombination mechanisms

The reactions most likely to be important in a water-catalyzed recombination include the following in addition to Reactions (1) through (6) above:

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (7)$$

$$CO + HO_2 \rightarrow CO_2 + OH \qquad (8)$$

$$CO + OH \rightarrow CO_2 + H \qquad (9)$$

$$O_3 + H \rightarrow OH + O_2 \qquad (10)$$

$$OH + OH \rightarrow H_2O + O \qquad (11)$$

It should be noted that Reactions (7) and (8) constitute a cycle as do Reactions (9) and (10). Benson[12] has pointed out that Reaction (8)

(12) Benson, S.W., " The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, 1960, P. 461.

is probably fast and Reaction (10) is known to be very fast. Reaction

(9) has a heat of activation of at least 7 kcal[13] and Reaction (11)

(13) See Avramenko, L. I. and R.V. Kolesnikova, p.32 in " Advances in Photochemistry", Vol. 2, Interscience Publishers, N.Y. 1964.

is known to be very fast also. The exact recombination mechanism may involve all these reactions as well as others of a similar nature.

Significance for Radiation Chemistry of CO_2

Harteck and Dondes[14,15] and others[16] have investigated

(14) Harteck, P. and Dondes, S., J. Chem. Phys. 23, 902 (1955)

(15) Ibid., 26, 1727 (1957)

(16) For general reference see Lind, S.C., " Radiation Chemistry of Gases", Reinhold Publishing Corp., N.Y. 1961, pp. 116-123.

the effects of ionizing radiation on CO_2 and found that CO_2 was not dissociated. A recombination mechanism similar to the one given above could obviously explain such a result, although the nature of the ionizing radiation may favor an ion mechanism or some other alternate process, as suggested by Harteck and Dondes.

Significance for The Venus Atmosphere

It is evident that an H-atom or OH-catalyzed recombination mechanism could explain the peculiar composition of the Venus atmosphere, namely the high abundance of CO_2 with no more than a trace of either CO or O_2.[17] These constituents might be expected to be present in the

(17) Harteck, P., Reeves, R.R., Jr., and Thompson, B.A., " Photochemical problems of the Venus Atmosphere", NASA Techanical Note TN-D-1984 (1963)

Venus atmosphere in relatively high concentrations due to photodissociation of CO_2. Other sources, such as photodissociation of water vapor to produce oxygen, and accumulation of carbon monoxide from volcanic exhalations have also been considered.

The most recent spectroscopic investigations[18] from

---

(18) Bottema, M., Plummer, W., and Strong, J., Astrophys. J. 139, 1021 (1964)

---

a balloon indicate the presence of trace amounts of atmospheric water vapor. For the above mechanism only very small amounts of water need be present. Photodissociation of the water would produce OH radicals and H-atoms which could be expected to be present in steady-state down to the cloud layer. It is probable, therefore that any oxygen or carbon monoxide formed in the Venus atmosphere react to regenerate CO_2 in the manner described above. Any excess carbon monoxide present could react to form carbon suboxide which may be a constituent of the observed cloud layer[19]. These reaction schemes thus provide an explanation for the

---

(19) Harteck, P. and Groth, W., Discussed by G.P. Kuiper in "The Threshold of Space", M. Zelikoff, Ed., Pergamon Press, London, 1957, p.85.

---

absence of both CO and O_2 from the Venus atmosphere in the abundances which might have been anticipated.

Acknowledgement

This work was carried out under a research grant from the National Aeronautics and Space Administration.

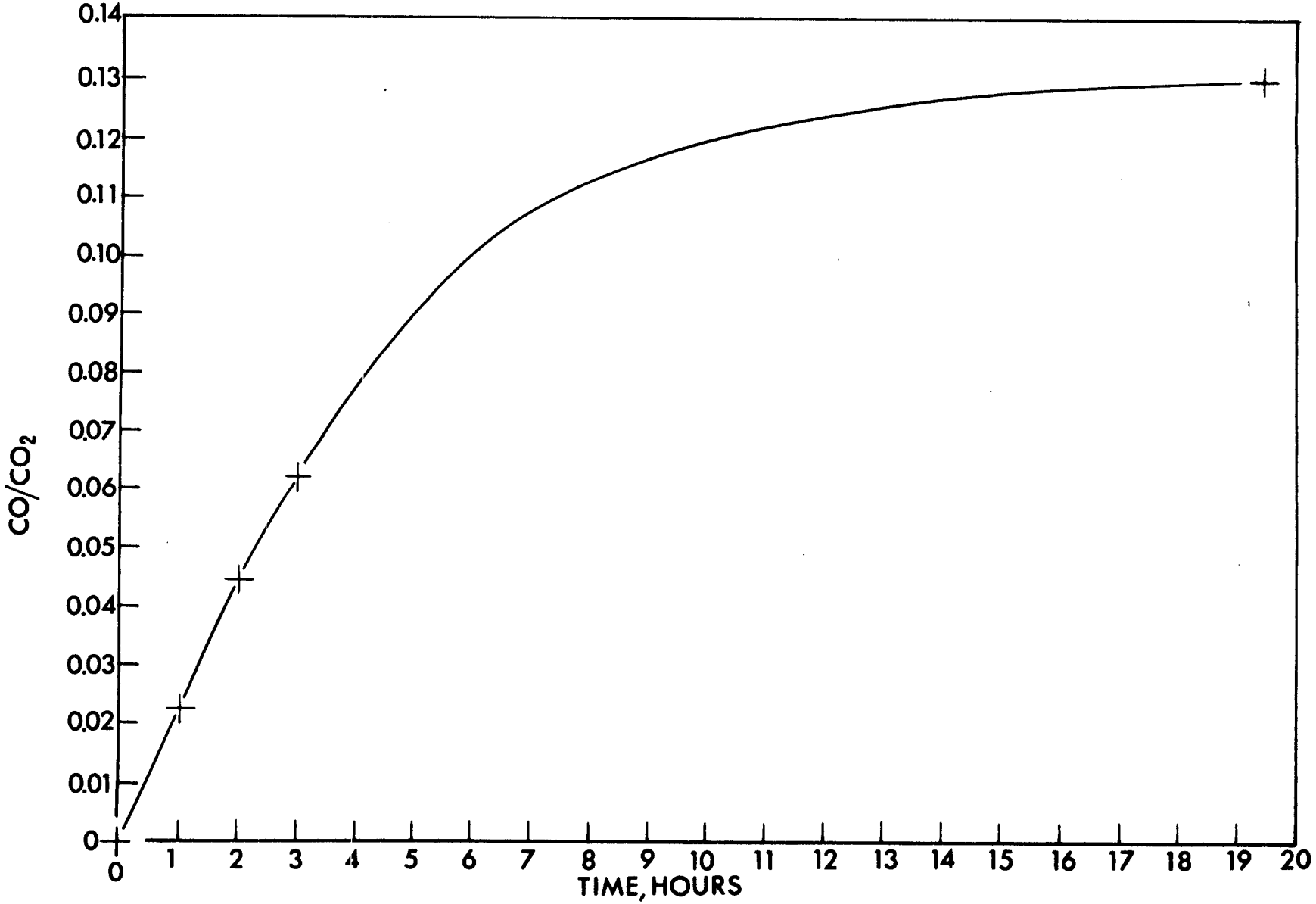

FIGURE 1 TYPICAL DISSOCIATION CURVE FOR CO_2 IRRADIATED WITH BROMINE LAMP